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PRESSURE AND TEMPERATURE DEPENDENT DEFLAGRATION RATE MEASUREMENTS OF LLM-105 AND TATB BASED EXPLOSIVES

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ABSTRACT

The pressure dependent deflagration rates of LLM-105 and TATB based formulations were measured in the LLNL high pressure strand burner. The role of binder amount, explosive type, and thermal damage and their effects on the deflagration rate will be discussed. Two different formulations of LLM-105 and three formulations of TATB were studied and results indicate that binder amount and type play a minor role in the deflagration behavior. This is in sharp contrast to the HMX based formulations which strongly depend on binder amount and type. The effect of preheating these samples was considerably more dramatic. In the case of LLM-105, preheating the sample appears to have little effect on the deflagration rate. In contrast, preheating TATB formulations causes the deflagration rate to accelerate and become erratic. The thermal and mechanical properties of these formulations will be discussed in the context of their pressure and temperature dependent deflagration rates.

INTRODUCTION

The decomposition kinetics and deflagration rates of energetic materials are important to the performance and safety of the material, especially in cook-off scenarios. Insensitive high explosives (IHE) are of particular interest to the explosives community because of they are less sensitive to thermal or impact stimuli relative to conventional HE's (e.g. HMX or RDX). TATB is the current material of choice for IHE formulations, however, testing of a new explosive, 2,6-Diamino-3,5-dinitropyrazine-1-oxide (commonly referred to as LLM-105), indicates that this materials may eventually become a superior candidate for IHE applications.

Deflagration rate measurements are important in the safety assessment of materials. Both thermal and mechanical stimuli can initiate a reaction in an energetic material. In insulated and/or contained environments, the pressure and temperature can rise quickly as the material reacts resulting in an acceleration of the reaction until runaway conditions are reached. Accurate knowledge of the reaction rates at conditions typical of those in accelerating reactions is necessary to understand and predict the violence of the ensuing explosion. Hydrodynamic calculations indicate that reacting materials can achieve pressures in the hundreds of MPa range (several kbar) and higher. Therefore, measurements of the laminar deflagration rate at these pressures are particularly important in safety assessment and predictive modeling.

Preheating samples to various temperatures and durations allows for thermal damage to the material prior to burn ignition. Depending on the nature of the sample, preheating can result in phase transitions and introduce cracks, voids, and fissures. Sometimes, the damage induced by preheating can be subtle and not easily predicted based on conventional thermal analysis techniques (e.g. DSC or TMA), yet the changes in the burn behavior can be dramatic. Our results indicate that TATB is such a material and preheating changes the burn rate and predictability of the material burn considerably. In contrast, LLM-105 based formulations tend to remain unaffected by preheating and the burn rates are nearly the same as the ambient temperature burn rates. Possible mechanisms* for the accelerated burns in TATB-based formulations are discussed.

EXPERIMENTS AND CALCULATIONS

LLNL HIGH PRESSURE STRAND BURNER

        Deflagration rates are measured using the LLNL high pressure strand burner, shown in Figure 1. This experimental technique is described in detail in the literature.[1,2] Briefly, burns are performed under constant volume in an atmosphere of Argon. The pressure is measured in-situ throughout the burn and burn progress is monitored via silver break wires that are embedded within the sample. A typical sample consists of nine individual pellets (0.25 in diameter by 0.25 in tall) and 10 burn wires, the exterior surface is encapsulated by an organic-polymeric material to prevent flame spread down the sides. The sample is prepressurized to a desired pressure using Argon, the burn is initiated via an igniter train (igniter wire, $BKNO_3$ and a thin HNS pellet), and the sample burns resulting in a rise in pressure on the order of 3-5 times the initial pressure. Many towers may be burnt in order to investigate a pressure range of 10-600 MPa.
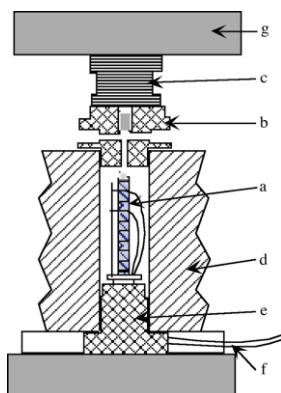
Figure 1. Strand burner schematic composed of a) nine segment burn sample with burn wires evenly spaced between segments (only two wires shown for clarity) and igniter on top, b) top plug with inlet and outlet ports and pressure transducer in center, c) load cell, d) pressure vessel, e) bottom plug with wire feed-throughs, f) signal wires to electronics, g) load frame (top and bottom).

        Typical pressure and flame front time-of-arrival data are shown in Figure 2. These results represent a well behaved burn because the wires are burned in order and the pressure rise stops after the last burn wire. The burn wire data should cover the time span of the pressure signal. Any significant deviation from this indicates anomalous behavior. For example, the report of all burn wires before the pressure reaches a maximum indicates that the deflagration front passes rapidly down the sample and leaves still-reacting material behind. This behavior is indicative of flame spread through the sample or of propagation of the flame down the side of the sample; although the epoxy coating should inhibit the latter.
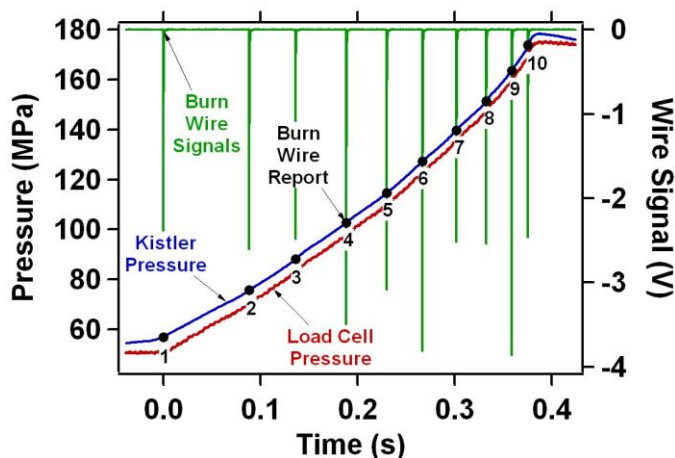
Figure 2. Typical strand burner data, showing temporal pressure behavior and flame-front time-of-arrival signals resulting from the burn wires.

To calculate deflagration rate as a function of pressure, the length and time-of-arrival for each pair of pellets is used, and the corresponding average pressure for this segment of the sample is calculated. The temporal pressure data can be used to calculate vivacity and surface area.[3-5]

MATERIALS

Two different formulations of LLM-105 were studied in this work and are listed in Table 1. Both formulations were prepared from the same lot of LLM-105 (LLNL number PP-XV-89A). Typically a formulation contains about 28% ground (0.1 – 10 μm, bimodal distribution with maximum population at 0.27 μm and 2.9 μm) and 72% unground (10 – 110 μm, maximum population at 42 μm) particles. The theoretical maximum density (TMD) for each formulation was calculated assuming 4.8% 2,6-diamino-3,5-dinitropyrazine (ANPZ), a lower powered explosive that is a precursor in the synthesis of LLM-105. The calculated TMD for RX-55-AB and –AY are 1.9212 and 1.9096 g/cc, respectively. Both formulations were uniaxially pressed in a mechanical pressing die at 207 MPa (30 kPSI) and 105-110 °C (3x5 min dwell, 1 min break between dwells, 5 min heat soak prior to first dwell).

Four different formulations of TATB were studied and variables include the binder type, binder amount and source of TATB; these formulations are listed in Table 1. In particular, the recrystallization solvent was found to improve the quality and size of the TATB crystals significantly over methods employed in the wet- and dry-aminated procedures.[6] LX-17 and RX-03-GP were uniaxially pressed in a mechanical pressing die at 207 MPa (30 kPSI) and 105 – 110 °C (3x5 min dwell, 1 min between dwells). RX-03-GO-IL4 was uniaxially pressed in a mechanical pressing die at 207 MPa (30 kPSI) and 135-139 °C (3x3 min dwell, 1 min between dwells, 5 min heat soak prior to first dwell).

Table 1. Formulation details.

Formulation	Wt% LLM-105	Wt% binder	LLM-105 source	Binder type	Density (g/cc)	% TMD
RX-55-AB	92.5	7.5	See text	Kel-F 800	1.857 ± 0.002	96.7
RX-55-AY	94	6	See text	Viton A	1.835 ± 0.004	96.1
Formulation	**Wt% TATB**	**Wt% binder**	**TATB source**	**Binder type**	**Density (g/cc)**	**% TMD**
LX-17	92.5	7.5	Wet-aminated	Kel-F 800	1.898 ± 0.008	97.6
PBX-9502	95	5	Dry-aminated	Kel-F 800	1.887 ± 0.004	97.1
RX-03-GO-IL4	92.5	7.5	Ionic Liquid recrystalization (fine and course crystals)	Cytop A	1.898 ± 0.004	97.7
RX-03-GP	92.5	7.5	Ionic Liquid recrystalization (fine and course crystals)	Kel-F 800	1.905 ± 0.002	98.0

<u>CALCULATIONS</u>

Reactions taking place during the final explosion are, in situations that do not involve shock stimuli, deflagrative in nature. Therefore, measurement of deflagration rate at high pressures and temperatures provides necessary information on runaway reaction behavior. This information is summarized in the burn rate equation,

$$B = aP^n \qquad (1)$$

where B is the burn rate (mm/s), a is the burn rate coefficient (mm/s·MPa^n), P is the pressure (MPa) and n is the pressure exponent (dimensionless).

RESULTS AND DISCUSSION

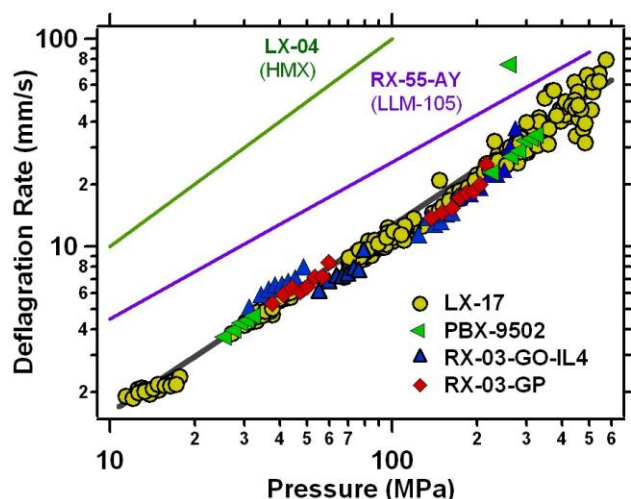<u>AMBIENT TEMPERATURE DEFLAGRATION RATE MEASUREMENTS</u>

The pressure dependent deflagration rates of the LLM-105 based formulations were measured between 0 and 300 MPa in a series of four burn-tower experiments. Prepresserization of the towers varied in order to achieve a wide pressure range for the set. Results of these experiments are plotted in Figure 3 along with the pressure dependent deflagration rate of LX-17 and LX-04 (85% HMX, 15% Viton A). The formulation burn rates are within error of each other and more experiments would, likely, produce better overlap. The RX-55-AY data at 40-80 MPa is more erratic than any of the other burns, which is tentatively attributed to minor, random errors (e.g. minor delamination of the organic encapsulation), and is not expected to be significant or reproducible under repeated testing. These results will be discussed below in the context of other material burn rates.
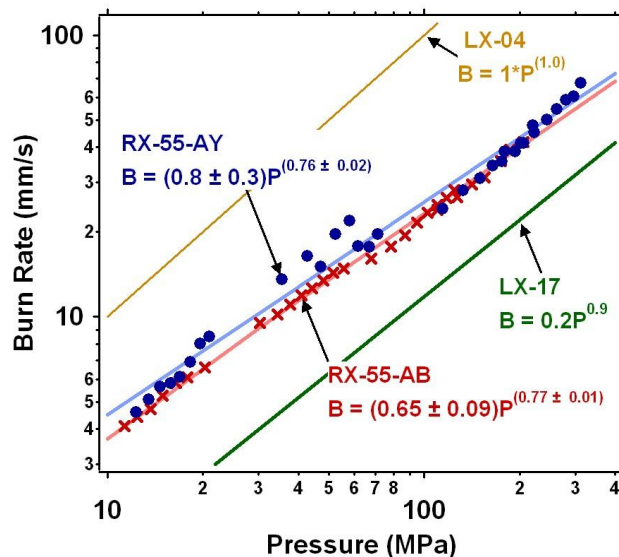
Figure 3. Pressure dependent deflagration rates for LLM-105 formulations. Refer to table 1 for formulation details.

Pressure dependent deflagration rates for all the TATB-formulations listed in Table 1 are show in Figure 4. LX-17 data was reported previously and is reproduced here.[7] Although there are a limited number of experiments of PBX-9502 and the two RX-03 formulations, all appear to burn in a well behaved manner and have similar burn rates to LX-17. The criteria for a well-behaved burn are discussed in the experimental section. In general, there are a variety of possible random errors that can occur during

a burn, however, the likelihood of significant random errors producing a well-behaved burn are small. Therefore, despite the limited number of experiments presented for each material in Figure 4, the orderly nature of the results indicate that this data is representative of an experiment that is free of significant random errors and reliable enough to draw preliminary conclusions.

Figure 4. Pressure dependent deflagration rates for TATB formulations. LX-17 data is reproduced from previous work.[7] Refer to Table 1 for formulation details.

In the ambient temperature burns of both the LLM-105 and TATB based formulations; one of the key observations is the laminar nature of the burns. Burns of HMX based formulations become extremely rapid and erratic at elevated pressure (>150 MPa), in a process termed deconsolidative burning. The hypothesized mechanism behind these wild burn rates is the physical deconsolidation of the material, which creates new cracks and voids and allows the flame to penetrate deep into the material. Materials that deconsolidatively burn at elevated pressures have been shown to be considerably more violent in confined heating experiments (i.e. cook-off scenarios).[8]

In HMX based materials, the binder type and volume fraction are important variables in determining if and when the material transitions to a deconsolidative burn. The mechanical properties of the material are heavily dictated by the binder type and amount, and studies have shown that increasing the binder amount increases the strain to failure and ultimate elongation[9] and decreases the likelihood of deconsolidation during burning.[1,2] LX-17 was shown previously to burn in a laminar fashion over a wide pressure range.[7] At this ratio of explosive to binder, a similar formulation made with HMX would deconsolidate above 150 MPa;[1] hence, the nature of the explosive, and, most likely, its burn temperature, play an important role in the deconsolidation. In the case of the LLM-105 formulations, the nature of the burn could not be predicted prior to experiments. The LLM-105 formulations both have relatively low binder content and the decomposition onset temperature (based on DSC results) indicates that LLM-105 is more thermally sensitive than TATB but less than HMX.[10]

In the case of the novel TATB formulations (RX-03 formulations), the change in binder and crystal morphology were not expected to affect the burn rate dramatically. Cytop A is a perfluorinated polymer with a room-temperature ultimate strength and Young's Modulus that are between those of Viton A and Kel-F 800.[9] In addition, atomistic simulations predict that Cytop A will adhere to the TATB crystals better than Kel-F 800;[11] presumably this will reduce the likelihood of cracks forming between the binder and TATB. Hence, the stable, laminar burns observed for both RX-03 formulations are not surprising.

ELEVATED TEMPERATURE DEFLAGRATION RATE MEASUREMENTS

Figure 5 shows the results of burning LLM-105 and TATB-formulations at elevated temperatures after thermally soaking the sample. In these measurements, the experiment was assembled, the sample

was heated to a desired temperature (typically 1 -2 °C/min), held for a desired length of time, and burned hot. The LX-17 experiments at 225 °C, which are reproduced here from a previous study,[7] were all heated and then pressurized, all the other experiments were pressurized first, then heated. For some materials, the order of heating and pressurizing can be important if there are material phase transitions that can occur under one set of conditions but not the other.[1] In the case of TATB and LLM-105, there are no known phase transitions in this temperature-pressure regime and the order of heating and pressurizing is not expected to affect the results. In addition, the LX-17 experiments at 225 °C were performed using band heaters around the pressure vessel and a small internal coil heater inside the pressure vessel (surrounding but not contacting or constricting the sample). The coil heater was later found to produce temperature gradients along the deflagration sample that spanned 16 °C[12] and was not used for any of the other experiments. In the coil-heater experiments, this temperature gradient can dramatically affect the experiment if the temperature spans a material phase transition or chemical decomposition.[12] In the case of LX-17, 225 °C is well below any decomposition or phase transition, hence this 16 °C gradient is not expected to play a major role in the deflagration behavior. However, further work is underway to repeat some of these experiments without the coil heater.
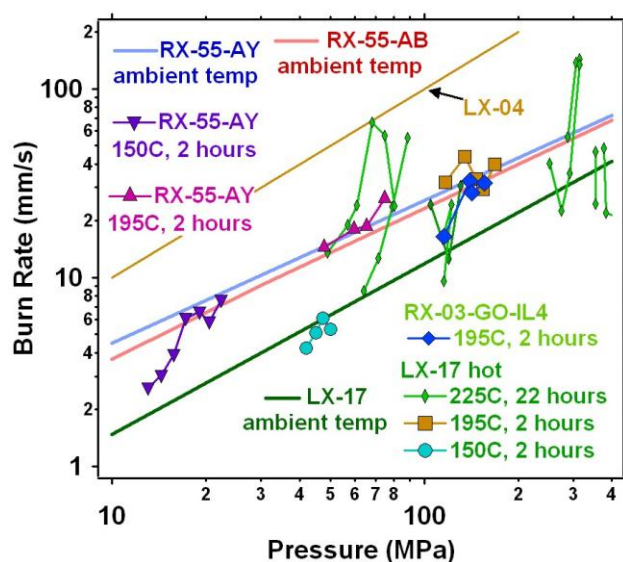
Figure 5. Deflagration rates of LLM-105 and TATB formulations after heating (burns were initiated at the temperatures listed). LX-17 burns at 225 °C are reproduced from previous work.[7] Refer to Table 1 for formulation details.

Heated deflagration rate measurements are particularly important to scenarios where an energetic material may have been thermally damaged and begins to cook-off. Previous studies of HMX based explosives demonstrate that heating the material above the β - δ phase transition of ca. 170 °C causes the material to burn at considerably higher rates. Burns of the same material below the β - δ phase transition, however, tend to behave similarly to ambient temperature burns.[1] These changes in burn rates are attributed to changes in the material structure rather than intrinsic changes in the decomposition and deflagration chemistry of the different phases.[13]

Neither TATB nor LLM-105 has any major phase changes below the decomposition temperature, making the choice of temperatures somewhat arbitrary. In the case of LLM-105 under heated conditions, our preliminary experiments indicate that the material burn rate does not change upon heating. The 22 hour, 225 °C burns of LX-17 were presented previously and it is clear that the material burns considerably faster and more erratically than the ambient temperature burns.[7] One could attribute some of this erratic burn behavior to the thermal gradients resulting from the coil heater. However, our preliminary data show that even under milder conditions (i.e. 2 hours at 195 °C) when only the band heaters were used (i.e. no coil heater, no thermal gradients), TATB formulations burn rapidly and erratically. Interestingly, when LX-17 was heated to 150 °C for 2 hours the sample burned much like an ambient temperature experiment.

The effect of the crystal quality and binder type (Cytop A vs. Kel-F 800) in the deflagration behavior at elevated temperature is more difficult to predict. Further experiments are necessary to conclude whether these two variables affect the deflagration behavior and major conclusions should be withheld until these experiments can be reproduced. However, one might expect that changing the binder will not ameliorate the erratic nature of the burn at elevated temperatures. At 195 °C, the sample is well above the glass transition of both binder materials (ca. 108 °C for Cytop A and 30 °C for Kel-F) and above the melt transition for Kel-F 800 (ca. 95 °C); no melt transition has been observed for Cytop A.[14,15]} Thus, the binder properties at 200 – 225 °C are expected to be similar for these two materials.

Previously, Koerner et al provided two possible explanations for why LX-17 burns erratically after 22hrs at 225 °C: either the anisotropic thermal expansion of TATB creates voids and cracks, or the elevated temperature assists in surmounting the energy barrier to decomposition causing an acceleration in the deflagration kinetics.[7] Based on our results of both LLM-105 and TATB formulations, the first hypothesis seems more plausible. Koerner et al. used the following basic Arrhenius analysis to estimate a chemical-decomposition rate at ambient and elevated temperature

$$\frac{k_2}{k_1} = \exp\left[\frac{-E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right]$$

where k_1 and k_2 are the chemical-decomposition rates, E_a is the activation energy, R is the gas constant, and T_1 and T_2 are the flame temperatures at ambient and elevated temperatures, respectively.[7] The activation energy for LLM-105 and TATB are provided by Weese et al. (250 and 193 kJ/mol respectively)[10] and the flame temperatures are estimated using Cheetah 5.0 (3083 and 3283 K for LLM-105; 2267 and 2467 K for TATB).[16] The ratio of k_2/k_1 is 1.8 and 2.9 for LLM-105 and TATB respectively (using values for the formulations results in similar ratios), hence, based on this analysis one would expect TATB to accelerate by a factor of ca. 2.9 at 200 °C and LLM-105 burns to accelerate by a factor of 1.8 at 200 °C. Clearly the LLM-105 data is not accelerated at elevated temperatures, which makes the thermal expansion hypothesis more plausible. In addition, Weese et al. recently showed that the coefficient of thermal expansion, as well as the heat capacity and thermal conductivity/diffusivity are significantly larger for TATB formulations than LLM-105 materials. [10]

One notable trend in all the heated TATB burns was the fact that the wires often burned out of order. Figure 2 shows the basic criteria for a well behaved burn in which the wires burn in order and the pressure rise is well correlated with the wires, indicating that the material is burning in a sequential, laminar fashion. Figure 6 shows representative pressures and burn wire report times for three different conditions/materials. As shown in Figure 6a, heated HMX-based explosives usually burn rapidly but the wires burn in order and the pressure rise is consistent with the burn progress. In Figure 6b shows a representative wire/pressure data set for an HMX-based material during a deconsolidative burn. It is clear that the wires burn in order and, as the burn begins to accelerate, the pressure rise increases dramatically and the remaining wires burn extremely rapidly. Plotted in Figure 6c is the pressure/wire data for a representative TATB based explosive at 195 °C (these experiments used only the band heaters, no coil heaters, in order to avoid any potential problems with thermal gradients). In all the heated TATB based experiments, the wires burn out of order, however the pressure rise is usually relatively steady. This kind of scenario could occur if the flame is able to penetrate deeply into the sample without burning all the burn wires. A deep crack or fissure might create the path for the flame to penetrate, especially if the individual crystals anisotropically expand, there may be considerable changes in the packing arrangement of crystals and binders. Further studies are necessary to explore this hypothesis.
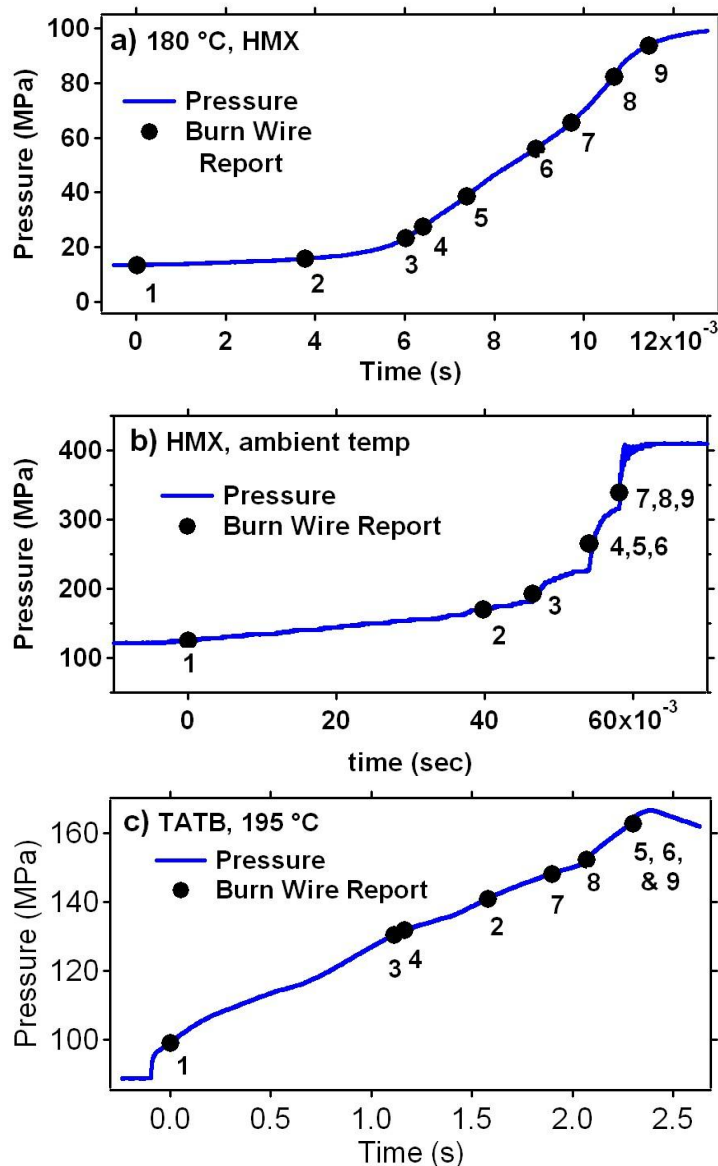
Figure 6. Pressure and burn wire report times for (a) a heated HMX-based material, (b) an elevated pressure, ambient temperature HMX-based material and (c) a heated TATB-based formulation.

SUMMARY AND CONCLUSIONS

The deflagration rates of LLM-105 and TATB based formulations are studied at various temperatures and pressures. This work is important in the assessment of safety and performance, in particular, in accidental heating scenarios (e.g. fires). The results of these studies indicate that neither material transitions to deconsolidative burning when the sample is ignited at ambient temperature. This observation is important because deconsolidative burning has been correlated with significant violence in cook-off experiments.[8] As was previous reported that, upon heating, LX-17 tends to burn significantly faster and more erratically than at ambient temperature.[7] A preliminary experiment on a novel TATB-formulation also produces this rapid and erratic burn behavior, although further work is necessary to draw any conclusions from this data. In contrast, heating the LLM-105 formulation prior to burning had little

effect on the burn rate. These results are important because they indicate that under fire situations, LLM-105 based materials may be more stable and reliable. Further work is necessary to fully understand the mechanism of accelerated burning in preheated LX-17 samples, however, our results in combination with previous studies of the material properties, indicate that the main factor may be changes the material that render it more prone to cracking and formation of pores and fissures.

ACKNOWLEDGEMENTS

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